



TITLE:

# Secondary decomposition of levoglucosan in pyrolytic production from cellulosic biomass

AUTHOR(S):

Kawamoto, Haruo; Morisaki, Hiroyuki; Saka, Shiro

---

CITATION:

Kawamoto, Haruo ...[et al]. Secondary decomposition of levoglucosan in pyrolytic production from cellulosic biomass. Journal of Analytical and Applied Pyrolysis 2009, 85(1-2): 247-251

ISSUE DATE:

2009-05

URL:

<http://hdl.handle.net/2433/240653>

RIGHT:

© 2008. This manuscript version is made available under the CC-BY-NC-ND 4.0 license <http://creativecommons.org/licenses/by-nc-nd/4.0/>; The full-text file will be made open to the public on 1 May 2011 in accordance with publisher's 'Terms and Conditions for Self-Archiving'; この論文は出版社版でありません。引用の際には出版社版をご確認ご利用ください。; This is not the published version. Please cite only the published version.

Title:

Secondary decomposition of levoglucosan in pyrolytic production from  
cellulosic biomass

Authors and affiliation:

Haruo Kawamoto\*, Hiroyuki Morisaki, Shiro Saka

\* Corresponding author: Tel/ Fax: +81-75-753-4737

Email address: [kawamoto@energy.kyoto-u.ac.jp](mailto:kawamoto@energy.kyoto-u.ac.jp) (H. Kawamoto)

Full postal address of the person to whom proofs are to be sent:

*Graduate School of Energy Science, Kyoto University  
Yoshida-honmachi, Sakyo-ku, Kyoto 606-8501, Japan*

**Abstract:**

Levogluconan (1,6-anhydro- $\beta$ -D-glucopyranose) is a major pyrolysis product from cellulose. To understand the secondary decomposition behavior in pyrolytic production of levogluconan from cellulosic biomass, influences of the pyrolysis vapor from wood or wood constituent polymers on the recovering process of levogluconan were studied at 400°C (30 mmHg). Japanese cedar (*Cryptomeria japonica*, a softwood) and Japanese beech (*Fagus crenata*, a hardwood) wood samples, cellulose, xylan (a hemicellulose) and the milled wood lignins isolated from the wood samples were used as the substances for production of the pyrolysis vapor. Since levogluconan and other substances were placed separately in a dual-space reactor to eliminate their direct contact, the interaction is expected in vapor-phase after volatilization of levogluconan and volatile formation from wood and related substances. Solid/liquid-phase interaction is also possible after condensation of the vapor on the reactor wall with lower temperature. The cellulose- and lignin-derived pyrolysis vapors reduced the recovery of levogluconan substantially, while the influences of the vapors from xylan and the substances containing xylan were comparatively very small. Such decomposition induced by the cellulose- and lignin-derived vapors was inhibited in the presence of the xylan-derived pyrolysis vapor.

**Keywords:**

Levogluconan; pyrolysis; secondary decomposition; cellulose; lignin; xylan; hemicellulose.

## Introduction

Levoglucosan (1,6-anhydro- $\beta$ -D-glucopyranose) is a potential chemical obtained from pyrolysis of cellulosic biomass [1]. The utilization in synthesis of various chemicals (especially chiral chemicals) and materials is very promising. Its unique chemical nature, i.e. 1,6-acetal ring and  $^1\text{C}_4$  conformation makes it an attractive chiral raw material [2]. Notably, the rigid conformation and the sterically hindered  $\beta$ -D-face of the molecule are advantageous for regioselective protection of the OH groups [2] and stereoselective functionalization [3]. Preparation of various biologically active compounds such as antibiotic macrolides [4-8] has been approached starting from levoglucosan [4-11]. Saccharification through rapid or vacuum pyrolysis of cellulosic biomass has also been proposed as a pretreatment method for ethanol fermentation [12-14]. Since the Pictet's report [15] in 1918, polymerization of levoglucosan has been studied extensively [16-19]. Many kinds of polysaccharides have been prepared from polymerization of levoglucosan [15-17] and its derivatives [18, 19].

Yield of levoglucosan from cellulosic biomass is known to be influenced by various factors [20-30]. Pyrolysis temperature and the inorganic impurities are the most important factors. Effective production of levoglucosan requires  $> 300^\circ\text{C}$  [20, 21]. Many papers have reported that only very small amounts of the inorganic impurities reduced the levoglucosan yield greatly [14, 22-25], although the mechanism has not been clarified yet. As a factor relating to cellulose itself, the levoglucosan yield increases with an increasing crystallinity of cellulose [26]. Some papers also

indicate the influences of other constituent polymers in cellulosic biomass; Hosoya et al. [27, 28] have reported that most of the identified volatile products from cellulose and lignin increased in their yields in pyrolysis of cellulose-lignin mixtures.

Mass- and heat-transfer efficiencies have also been discussed with the levoglucosan yield [29, 30]. The levoglucosan yield increases under vacuum conditions, since levoglucosan effectively vaporizes before suffering from the secondary reactions [29]. Fast pyrolysis conditions, which are characteristic in rapid heating and quick recovery of the product vapor, are also preferable in production of levoglucosan [30].

Accordingly, the relationships between the pyrolysis condition and the levoglucosan yield are well documented. However, it has not been discussed how coexisting pyrolysis products from cellulose and other cellulosic biomass affect the recovering process of levoglucosan. Levoglucosan is reported to be stabilized up to 350°C in some aromatic substances with high  $\pi$ -electron densities probably through complexation with the CH/ $\pi$  interaction [31]. Such alternation of the reactivity may be included in pyrolytic production of levoglucosan. Understanding the secondary decomposition behavior in the presence of other pyrolysis products will be useful to improve the pyrolytic production of levoglucosan.

In this paper, influences of the coexisting pyrolysis vapors from cellulose, xylan, lignin and wood on the secondary decomposition behavior of levoglucosan are studied at 400°C/ 30 mmHg. A dual-space reactor is useful to eliminate the direct solid-solid

interactions between levoglucosan and other substances.

## 2. Experimental

### 2-1 Materials

Levoglucosan was purchased from Tokyo Kasei Co. Japanese cedar (*Cryptomeria japonica*, a softwood) and Japanese beech (*Fagus crenata*, a hardwood) wood flours [ $< 80$  mesh, oven-dried ( $105^{\circ}\text{C}/24\text{ h}$ )] were used after extraction with ethanol/benzene (2:1, v/v) in a Soxhlet apparatus for 6 h. Cellulose powder (200-300 mesh, Toyoroshi Co.) and xylan from beech wood (Sigma Co.) were commercial available. The xylan sample was demineralized before pyrolysis by washing with 0.05 M HCl/MeOH at room temperature for 24 h twice and subsequently with MeOH repeatedly until the electronic conductivity of the washing become constant. Demineralized wood samples were also prepared in the same procedure. The milled wood lignins (MWL) were isolated and purified from Japanese cedar and Japanese beech wood samples according to the method in the literature [32]. The ash contents of these samples were negligible as indicated from the undetectable levels of residues in thermogravimetric analysis in air at  $600^{\circ}\text{C}$  (heating rate:  $10^{\circ}\text{C}/\text{min}$ ) with a Shimadzu TGA 50.

### 2-2 Heat-treatment in a dual-space reactor and product analysis

Pyrolysis was conducted with the experimental set-up in Fig. 1. A small

sample holder made of Pyrex glass (internal diameter: 4.0 mm, length: 8.0 mm, glass thickness: 1.0 mm) is placed at the bottom of a Pyrex glass tube (internal diameter: 10.0 mm, length: 300 mm, glass thickness: 1.0 mm). Crystalline levoglucosan (10 mg) was placed in the inner sample holder, and cellulose, xylan, lignin, or wood sample (10 mg) was placed at the bottom of the outer tube reactor. Accordingly, direct contact between levoglucosan and other substances is not possible in this reactor. Various mixtures (10 mg each) which include cellulose-xylan (5:3, w/w), cellulose-MWL (5:2, w/w), MWL-xylan (2:3, w/w) and cellulose-xylan-MWL (5:3:2, w/w) were also used. After the connection to an aspirator (30 mmHg), pyrolysis was started by inserting the reactor to a muffle furnace preheated at 400°C through a small hole from the top. During pyrolysis, levoglucosan vapor was mixed with the pyrolysis vapor from other substances as shown in Fig. 1 (vapor-phase interaction). Condensation of the vapor on the reactor wall with lower temperature was also observed, where liquid-phase interaction is expected.

After pyrolysis for 3 min, the reactor was immediately taken out of the furnace and cooled with flowing air for 1 min and then in cold water for 1 min. Inside of the reactor which included the inner sample holder was extracted with D<sub>2</sub>O (1.0 mL) to give a D<sub>2</sub>O-soluble portion. In this portion, levoglucosan and other polar substances were included. The D<sub>2</sub>O-soluble portion was analyzed with gel-permeation chromatography (GPC) under the conditions of column: Asahipak GS220HQ; eluent: water (1.0 mL/min); detector: RID; column temperature: 40°C. Recovery of levoglucosan was

determined by analyzing the D<sub>2</sub>O-soluble portion with <sup>1</sup>H NMR by using 2-furancarboxylic acid as an internal standard. The <sup>1</sup>H NMR measurement was conducted with a Bruker AC-400 (400MHz) spectrometer, and the chemical shifts are shown in  $\delta$  (ppm) with sodium 3-(trimethylsilyl)-1-propanesulfonate as an internal standard. The yields of levoglucosan was calculated from comparing the peak area of the signal at  $\delta$  5.1 (C<sub>1</sub>-H of levoglucosan) with those of 2-furancarboxylic acid. The wood and cellulose samples also produced levoglucosan, and hence, these amounts were subtracted from those determined in this method.

### *2-3 Heat treatment of levoglucosan-pyrolysis product mixture*

In pyrolysis with the dual-space reactor (described above), pyrolysis vapors condensed on the reactor wall with the temperature less than 250°C (Fig. 2). To evaluate the influences after condensation, heat-treatment of various mixtures of levoglucosan and the pyrolysis products (condensates) from other substances were conducted.

The pyrolyzates (condensates) from the wood samples or the constituent polymers were obtained by pyrolysis of these substances (10 mg each) in the reactor without inner sample holder (400°C/ 30 mmHg/ 3 min). The condensates formed on the upper side of the reactor wall were extracted with methanol (0.8 mL). After the methanol solution was mixed with levoglucosan (10 mg), the resulting solution was taken into another Pyrex glass tube reactor and evaporated *in vacuo*. Before pyrolysis,



the reactor was connected to a N<sub>2</sub> bag through a three-way tap, and the air inside the reactor was exchanged with N<sub>2</sub>. Heat-treatment was conducted by inserting the reactor into the muffle furnace (150, 200 or 250°C) for 3 min. The analytical methods of the products were similar to those described above.

### 3. Results and discussion

As shown by the pictures of the reactors and the temperature distribution of the reactor wall (Fig. 2), yellow to dark brown condensates were formed at the upper side of the reactor wall < 250°C, except for the control (only levoglucosan) and xylan experiments, which gave colorless and pale yellow condensates, respectively. Some parts of the condensates with dark brown color were not soluble in D<sub>2</sub>O and other solvents. These insoluble materials (char) were also formed in the absence of levoglucosan. Secondary carbonization of the pyrolysis vapors from wood and the constituent polymers proceeds after condensation on the reactor wall, along with the primary char formation at the bottom of the tube reactor. No char was observed inside the inner sample holder under all experimental conditions.

Fig 3 summarizes the recoveries of levoglucosan under the influences of the pyrolysis vapors from wood and the constituent polymers. These recoveries do not include the amounts of levoglucosan formed from cellulose and wood samples. Unexpectedly, levoglucosan in the control experiment was almost quantitatively recovered (97.4%) as a colorless condensate at 400°C/ 30 mmHg. Thus, volatilization

of levoglucosan with the estimated boiling point around 300°C [33] effectively occurs before the secondary decomposition takes place.

In the presence of the pyrolysis vapors from the wood samples, this recovering process of levoglucosan was not influenced greatly [levoglucosan recovery: 91.0 % (cedar); 82.9 % (beech)]. The influence of the xylan-derived pyrolysis vapor was also small (levoglucosan recovery: 91.6 %). In contrast the pyrolysis vapors from the cellulose and MWLs (cedar and beech) reduced the recoveries down to 37.2, 61.3 and 64.4 %, respectively. These influences were not dependent on the wood species, i.e. softwood and hardwood.

These results imply an important suggestion in pyrolytic production of levoglucosan. For effective production of levoglucosan, pure cellulose is generally used to avoid the secondary reactions, since the impurities such as inorganic substances substantially reduce the levoglucosan yield. The present results, however, suggest that some of the levoglucosan molecules formed from cellulose are decomposed under the influence of other pyrolysis products from cellulose. The lignin-derived vapor also causes the secondary decomposition. Since direct contact between levoglucosan and cellulose or MWL is not possible in the dual-space reactor, such secondary decomposition would proceed in vapor-phase or liquid/solid-phase after condensation.

Thermal polymerization [15, 16] is a possible secondary reaction which reduces the levoglucosan recovery. Pictet [15] have reported that levoglucosan polymerizes at > 240°C, which is much lower than the present temperature (400°C). Fig 4 shows the

results of GPC analysis of the D<sub>2</sub>O-soluble portions of the condensates. In the chromatogram (control), only a very small signal (9.2 min) is observed in higher molecular weight (MW) (shorter retention time) region, along with a large signal assigned to levoglucosan. Accordingly, pure levoglucosan effectively vaporizes under the present heat-treatment conditions before the thermal polymerization proceeds. The signal at 9.2 min increases slightly in the chromatogram obtained in the presence of the MWL (cedar)-derived vapor. The MWL (beech) gave a similar result. Although cellulose itself gave some broad signals at high MW region without addition of levoglucosan, the signals from levoglucosan in the presence of the cellulose-derived vapor are observed at much higher MW region. Consequently, the cellulose-derived pyrolysis vapor accelerates the thermal polymerization of levoglucosan. This activation is much more effective than the lignin-derived pyrolysis vapor. It is also noted that levoglucosan polymerization was not effective with the wood samples, even though these include cellulose and lignin as the constituent polymers.

Demineralization by acid-washing slightly reduced the levoglucosan recoveries (cedar: 91.0 to 82.2%; beech: 82.9 to 75.6%). However these recoveries are still larger than that with cellulose or lignin. [Fig 5](#) summarizes the levoglucosan recoveries in the experiments with various mixtures of wood constituent polymers. The recoveries in the presence of the cellulose-MWL mixtures are explainable just as sum of the results with cellulose and MWL ([Fig. 3](#)). Contrary to this, the addition of xylan substantially increased the levoglucosan recoveries [cellulose-xylan: 73.8%; MWL (beech)-xylan:

91.9%; cellulose-xylan-MWL (beech): 90.4%] as compared with the results of the original substances [cellulose: 37.2%; MWL (beech): 64.4%; cellulose + MWL (beech): 47.9%]. The levoglucosan recoveries in the presence of the MWL-xylan and cellulose-xylan-MWL mixtures were rather equivalent to those of the wood samples. Accordingly, the xylan-derived vapor inhibits the decomposition of levoglucosan, which is induced by the cellulose- and lignin-derived vapors. Relatively small influences of the wood samples are explainable with such action of the xylan-derived vapor.

To obtain the information about the influences of the pyrolysis vapors after condensation on the reactor wall, levoglucosan was heated at 150-250°C in N<sub>2</sub> (1atm) for 3 min with the pyrolysis products (condensates) from the wood samples and the constituent polymers. At 150 and 200°C, levoglucosan was completely recovered even in the presence of the pyrolyzates. By increasing the temperature up to 250°C, the levoglucosan recovery was lowered under the influences of the pyrolyzates probably through the secondary decomposition (Fig. 6). In this type of experiments, the pyrolyzates from the substances containing xylan [wood and the cellulose + xylan + MWL mixture] also exhibited only small influences on the levoglucosan recovery, as compared with the results with the pyrolyzates from cellulose, MWL (beech) and their mixture (levoglucosan recovery: 63.7, 43.9 and 34.2%, respectively).

Transglycosilation is a common reaction in pyrolysis of glycosides and polysaccharides [20, 21, 34]. Thermal polymerization of levoglucosan proceeds similarly through ring-opening of the glycosidic 1,6-acetal bond. Although the

transglycosilation mechanism in pyrolysis is still controversial between homolytic vs. heterolytic mechanisms [20], the ring-opening polymerization is expected to be accelerated with acid catalysis, assuming the polymerization to proceed in the heterolytic mechanism. However, the pHs of the aqueous solutions of the condensates from pyrolysis of cellulose, xylan and beech wood (5 mg each) in water (0.5 ml) were not so different (around pH 4). Accordingly, the different influences of the pyrolysis vapors from cellulose, xylan and wood are not explainable only with the acidities of the pyrolyzates.

The present results are explained more reasonably by considering a radical mechanism, although the mechanism is not clear presently. Some radical-induced decomposition of levoglucosan would occur in the presence of the pyrolysis vapors of cellulose and lignin, and this is inhibited with the xylan-derived products. Hosoya et al. [35] have reported that levoglucosan decomposed in vapor-phase to CO and CO<sub>2</sub> at 400°C, and this decomposition was effectively inhibited in the presence of the aldehyde-type compounds. Furthermore, from the clearly observed isotope effect with the deuterium-labeled acetaldehyde, they concluded that this inhibition arises from the H-donation from the aldehyde-H to some reactive radical intermediates. Pictet has reported that the polymerization of levoglucosan occurred at much lower temperature in the presence of platinum black catalyst, although they did not discuss the reason [15]. This catalysis cannot be explained only with the heterolytic ring-opening polymerization mechanism.

## 4. Conclusions

Levoglucosan was almost quantitatively recovered as a colorless condensate on the reactor wall < 250 °C at 400°C under a mild vacuum condition (30 mmHg). The influences of the pyrolysis vapors from wood and the constituent polymers on this recovering process were clarified with a dual-space reactor. As summarized in Fig. 7, the pyrolysis vapors from cellulose and lignin induced the secondary decomposition of levoglucosan, while the influences of the xylan- and wood-derived vapors were comparatively small. Furthermore, the xylan-derived vapor was found to inhibit the decomposition which is induced by the cellulose- and lignin-derived vapors. Similar relationships were also observed in heat-treatment [N<sub>2</sub> (1 atm) at 250°C] of the mixtures of levoglucosan and the pyrolyzates. Although the mechanisms are not clear presently, the present results are explained more reasonably by introducing a radical mechanism for such induced levoglucosan decomposition. The present observations will be useful for improving the pyrolytic production of levoglucosan.

## References

- [1] D. S. Scott, J. Piskorz, D. Radlein, Levoglucosenone and levoglucosans, Z. J. Witczak ed., ATL press, Mount Prospect, 1994, 179.
- [2] Z. J. Witczak, Levoglucosenone and levoglucosans, Z. J. Witczak ed., ATL press, Mount Prospect, 1994, 165.

- [3] Z. J. Witczak, ACS Symposium Series 954, Materials, chemicals and energy from forest biomass, D. S. Argyropoulos ed., ACS Books, Washington, 2007, 332
- [4] V. Bailliez, R. M. de Figueriredo, A. Olesker, J. Cleophax, Tetrahedron Lett. 44 (2003) 9151.
- [5] C. M. J. Fox, R. N. Hiner, U. Warriar, J. D. White, Tetrahedron Lett. 29 (1988) 2923.
- [6] A. F. Sviridov, V. S. Borodkin, M. S. Ermolenko, D. V. Yashunsky, N. K. Kochetkov, Tetrahedron 47 (1991) 2291.
- [7] N. K. Kochetkov, D. V. Yashunsky, A. F. Sviridov, M. S. Ermolenko, Carbohydr. Res. 200 (1990) 209.
- [8] T. Wakamatsu, H. Nakamura, E. Naka, Tetrahedron Lett. 27 (1986) 3895.
- [9] P. Boquel, C. Taillefumier, Y. Chapleur, P. Renaut, S. Samreth, F. D. Bellamy, Tetrahedron 49 (1993) 83.
- [10] V. N. Kālè, D. L. J. Clive, J. Org. Chem. 49 (1984) 1154.
- [11] V. Bailliez, A. Olesker, J. Cleophax, Tetrahedron 60 (2004) 1079.
- [12] F. Shafizadeh, T. T. Stevenson, J. Appl. Polym. Sci. 27 (1982) 4577.
- [13] E.M. Prosen, D. Radlein, J. Piskorz, D. S. Scott, R. L. Legge, Biotechnol. Bioeng. 42 (1993) 538.
- [14] J. Piskorz, D. S. A. G. Radlein, D. S. Scott, S. Czernik, J. Anal. Appl. Pyrol., 16 (1989) 127.
- [15] A. Pictet, Helv. Chim. Acta 1 (1918) 226.
- [16] M. L. Wolfrom, A. Thompson, R. B. Ward, J. Am. Chem. Soc. 81 (1959) 4623.

- [17] M. L. Wolfrom, A. Thompson, R. B. Ward, D. Horton, R. H. Moore, *J. Org. Chem.* 26 (1961) 4617.
- [18] C. Schuerch, *Adv. Carbohydr. Chem. Biochem.* 39 (1981) 157.
- [19] N. K. Kochetkov, *Tetrahedron* 43 (1987) 2389.
- [20] M. J. Antal, Jr., *Adv. Solar Energy* 1 (1983) 61.
- [21] F. Shafizadeh, *J. Anal. Appl. Pyrol.*, 3 (1982) 283.
- [22] F. Shafizadeh, R. H. Furneaux, T. G. Cochran, J. P. Scholl, Y. Sakai, *J. Appl. Polymer. Sci.* 23 (1979) 3525.
- [23] G. N. Richards, G. Zheng, *J. Anal. Appl. Pyrol.*, 21 (1991) 133.
- [24] N. Shimada, H. Kawamoto, S. Saka, *J. Anal. Appl. Pyrol.*, 81 (2008) 80.
- [25] H. Kawamoto, D. Yamamoto, S. Saka, *J. Wood Sci.* 54 (2008) 242.
- [26] O.P. Golova, A.M. Pakhomov, E.A. Andrievskaya, R.G. Krylova, *Dokl. Akad. Nauk, SSSR* 115 (1957) 1122.
- [27] T. Hosoya, H. Kawamoto, S. Saka, *J. Anal. Appl. Pyrol.*, 80 (2007) 118.
- [28] T. Hosoya, H. Kawamoto, S. Saka, *J. Anal. Appl. Pyrol.*, submitted.
- [29] F. Shafizadeh, Y. L. Foo, *Carbohydr. Res.* 29 (1973) 113.
- [30] C. I. de Jenga, M. J. Antal, Jr., M. Jones, Jr., *J. Appl. Polym. Sci.* 27 (1982) 4313.
- [31] T. Hosoya, H. Kawamoto, S. Saka, *Carbohydr. Res.*, 341 (2006) 2293.
- [32] A. Bjorkman, *Svensk papperstidn* 59 (1956) 477.
- [33] I. Milosavljevic, V. Oja, E. M. Suuberg, *Ind. Eng. Chem. Res.*, 35 (1996) 653.
- [34] A. Ohnishi, H. Sugisawa, *Kagaku no Ryoiki*, 30 (1976) 84.



- [35] T. Hosoya, H. Kawamoto, S. Saka, J. Anal. Appl. Pyrol., in press  
(doi:10.1016/j.jaap.2008.06.008).

## Legend of figures

Fig. 1 The experimental set-up and the expected vapor- and liquid-phase interactions between levoglucosan and the volatile products from wood and the constituent polymers.

Fig. 2 Pictures of the reactors (upper side) after heat-treatment with the temperature profile of the reactor wall (400°C/ 30mmHg/ 3 min).

LG: levoglucosan.

Fig. 3 Influences of various pyrolysis vapors on recovery of levoglucosan (400°C/ 30mmHg/ 3 min).

The amounts of levoglucosan formed from wood and cellulose are not included.

LG: levoglucosan.

Fig. 4 Gel-permeation chromatograms of the D<sub>2</sub>O-soluble portions of the condensates obtained from levoglucosan (control) and levoglucosan in the presence of the pyrolysis vapor of cellulose or MWL (cedar) (400°C/ 30mmHg/ 3 min).

LG: levoglucosan.

Fig. 5 Influences of the pyrolysis vapors from various mixtures on recovery of

levoglucosan (400°C/ 30mmHg/ 3 min).

The amounts of levoglucosan formed from the mixtures containing cellulose are not included.

Fig. 6 Recovery of levoglucosan in heat-treatment of the mixtures of levoglucosan and the pyrolyzates (condensates) from wood and the constituent polymers [250°C/ N<sub>2</sub> (1 atm)/ 3 min].

The amounts of levoglucosan formed from wood and other substances containing cellulose are not included.

LG: levoglucosan.

Fig. 7 Influences of the pyrolysis vapors from wood constituent polymers on secondary decomposition of levoglucosan in pyrolytic production from cellulosic biomass.

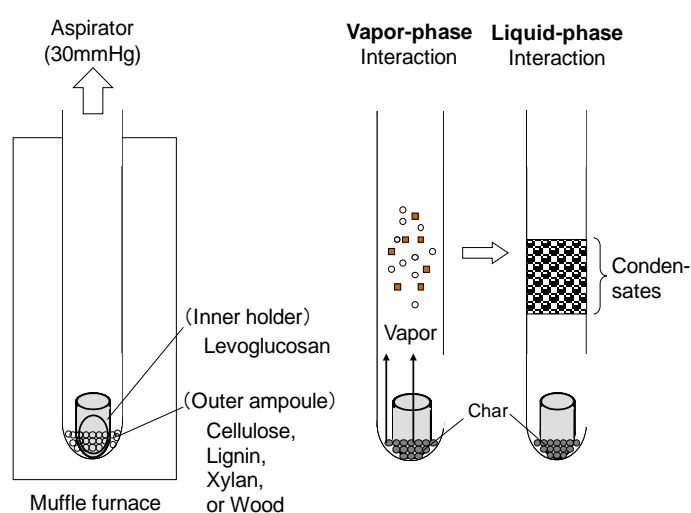


Fig. 1 The experimental set-up and the expected vapor- and liquid-phase interactions between levoglucosan and the volatile products from wood and the constituent polymers.

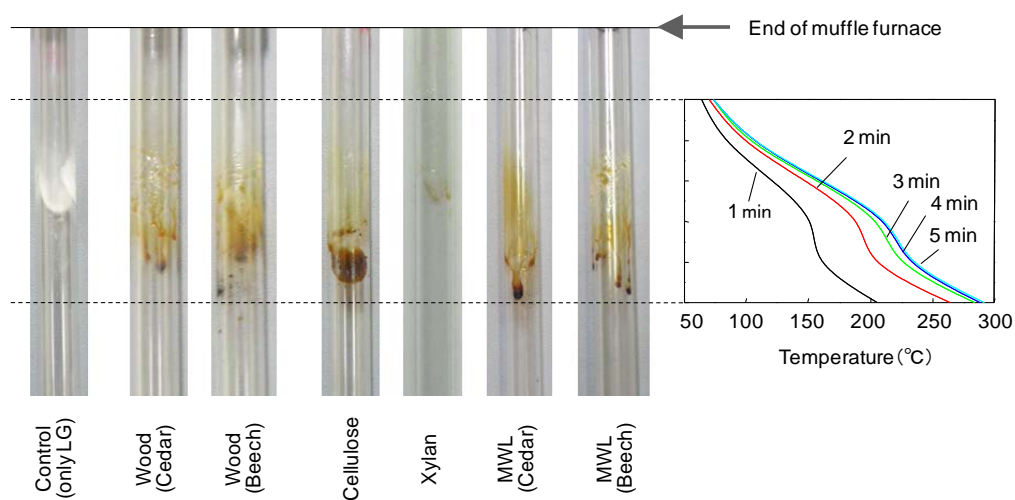


Fig. 2 Pictures of the reactors (upper side) after heat-treatment with the temperature profile of the reactor wall (400°C/ 30mmHg/ 3 min).

LG: levoglucosan.

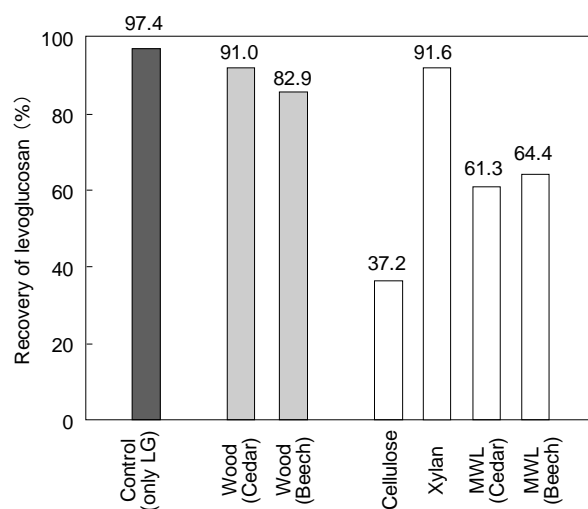


Fig. 3 Influences of various pyrolysis vapors on recovery of levoglucosan (400°C/ 30mmHg/ 3 min).

The amounts of levoglucosan formed from wood and cellulose are not included.

LG: levoglucosan.

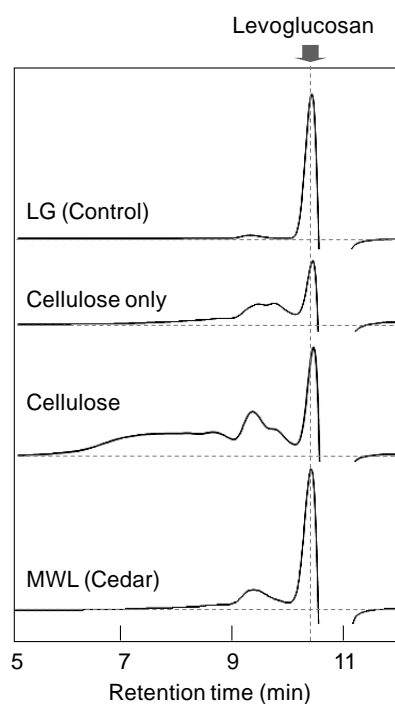


Fig. 4 Gel-permeation chromatograms of the D<sub>2</sub>O-soluble portions of the condensates obtained from levoglucosan (control) and levoglucosan in the presence of the pyrolysis vapor of cellulose or MWL (cedar) (400°C/ 30mmHg/ 3 min).

LG: levoglucosan.

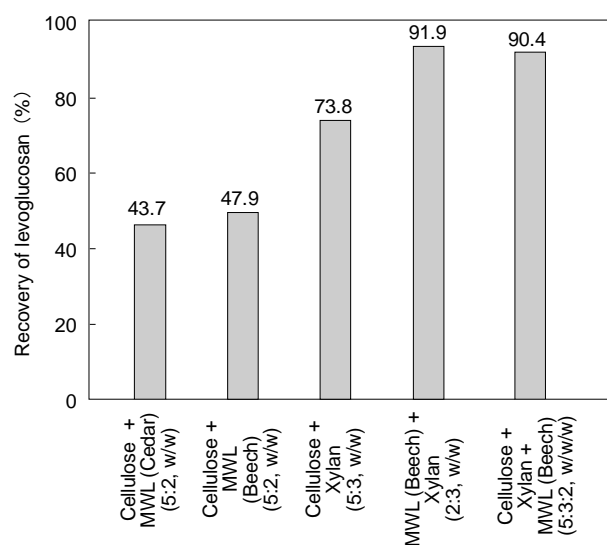


Fig. 5 Influences of the pyrolysis vapors from various mixtures on recovery of levoglucosan (400°C/ 30mmHg/ 3 min).

The amounts of levoglucosan formed from the mixtures containing cellulose are not included.



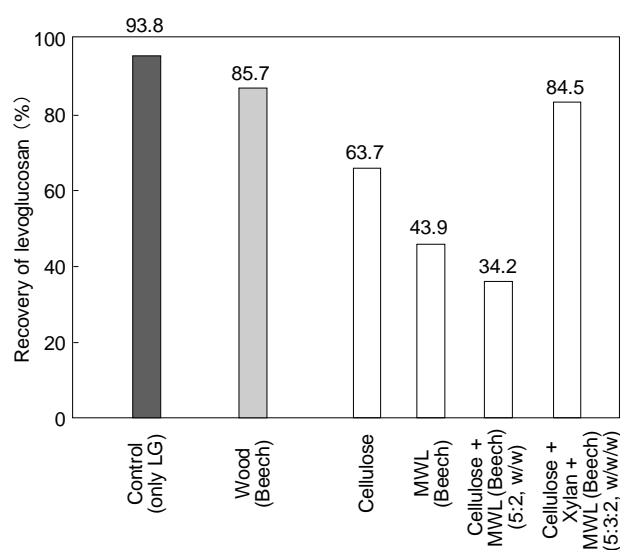


Fig. 6 Recovery of levoglucosan in heat-treatment of the mixtures of levoglucosan and the pyrolyzates (condensates) from wood and the constituent polymers [250°C/ N<sub>2</sub> (1 atm)/ 3 min].

The amounts of levoglucosan formed from wood and other substances containing cellulose are not included.

LG: levoglucosan

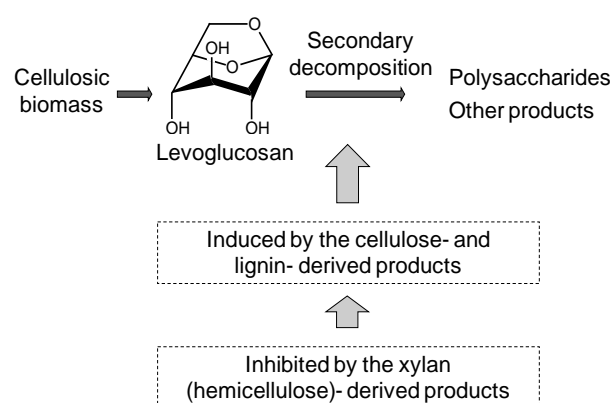


Fig. 7 Influences of the pyrolysis vapors from wood constituent polymers on secondary decomposition of levoglucosan in pyrolytic production from cellulosic biomass.